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PHOTOINDUCED ELECTRONIC ENERGY TRANSFER - THEORETICAL AND EXPERIMENTAL ISSUES FOR LIGHT HARVESTING APPLICATIONS

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Final Report

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14. ABSTRACT

Successful experimental and computational studies were carried out on electronic energy transfer in molecular systems subject to either coherent or incoherent light. Specific emphasis was placed on exposing and understanding the role of coherent dynamics in energy transfer, and its possible impact on the efficiency of light harvesting systems. Considerable insight into the fundamentals of these processes was obtained, and important new research directions were identified.

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Final Performance Report

Grant Title -- Photoinduced Electronic Energy Transfer: Theoretical and Experimental Issues for Light Harvesting Applications

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Stated aims of the project:

Electronic energy transfer (EET) within single molecules and amongst groups of molecules is a fundamental process in nature, central to a vast array of chemical, physical and biological phenomena. Recent experimental results have made clear that (i) the development of efficient solar collection devices requires fundamental studies of electronic energy transfer in order to gain a deeper |understanding of the nature of, and conditions for, facile EET, and (ii) basic experimental and theoretical studies on natural biological materials should provide deep insights into the unexpected, but welcome, role of quantum effects in enhancing EET in large |light harvesting systems. We intend to conduct forefront theoretical and experimental studies on molecular systems displaying electronic energy transfer. Formal studies will result in a high level theoretical approach to the exact dynamics of EET within donor-acceptor molecules and to computer programs to efficiently compute the dynamics of such systems. State-of-the-art two photon echo experiments will be conducted on a series of antenna proteins from marine cryptophyte algae to expose, and quantify, the role of quantum effects in EET in these naturally occurring systems. A high degree of collaboration between the experimental and theoretical groups involved in this project is expected to significantly enhance both aspects of this research, yielding a unified perspective on conditions for efficient and effective EET in light harvesting systems.

Summary of key results:

1. Coherence in photosynthetic light harvesting (experiment)

The initial step in photosynthesis involves the capture of energy from sunlight. Specialized pigment-protein complexes, called light-harvesting antenna complexes, have evolved for this purpose. The aim of our work was to elucidate how ultrafast energy transfer occurs in light harvesting, in particular the role of coherence. This topic has been prominent in recent experimental and theoretical studies. Owing to the complexity of the processes being examined, there has been much discussion among researchers about what is being measured by recent experiments and what does it mean.

The current surge of interest in coherent energy transfer dynamics stemmed from work employing two-dimensional electronic spectroscopy (2DES) to monitor the dynamics in the FMO complex from green sulfur bacteria. The increased sensitivity afforded by 2DES enabled a detailed study of the dynamics in these complex systems. Three groups (including ours) have reported the observation of oscillations in 2DES attributed to the coherent evolution of electronic excitations in photosynthetic proteins. Studies with the samples at cryogenic temperatures include the Fenna-Mathews-Olson (FMO) complex from green sulfur bacteria, reaction centers from purple bacteria, and the peripheral antenna complex LHCII from higher plants. That work has suggested that coherence may contribute to the functionality of light harvesting proteins.

In our laboratory we have studied the primary light harvesting complexes isolated from cryptophyte algae. Particularly striking results have been attained for phycocyanin 645 (PC645), isolated from *Chroomonas* CCMP270. PC645 is a phycobiliprotein, a light harvesting antenna protein found in the thylakoid lumen of cryptophyte algae, which contains eight bilins. PC645 contains three different types of bilins – two dihydrobiliverdins (DBV) with a peak absorption of 580 nm, two mesobiliverdins (MBV) with absorption peaks near 610 nm and four phycocyanobilins (PCB) two with peak absorptions of 630 nm and two with peaks at 645 nm – covalently bound to a protein matrix. The presence of three distinct types of chromophore increases the coverage of the solar spectrum available to these specific cryptophyte algae. From a spectroscopic perspective, this provides an opportunity to further quantify excitation dynamics in light harvesting systems. While there is still significant spectral overlap of the different bilins, the different chromophores predominantly absorb light

at different frequencies and allow a reasonably clear interpretation of dynamics as the information is more spectrally spread out. In PC645 the two DBV molecules that absorb on the blue side of the spectrum are positioned together in the center of the protein and have an electronic coupling of 320 cm^{-1}.

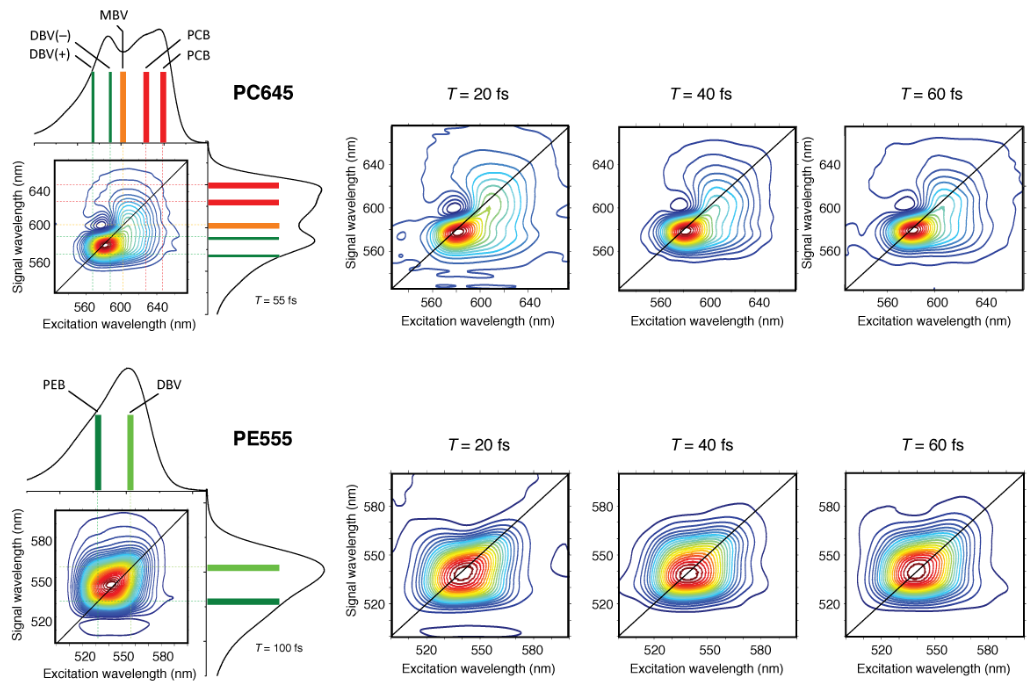

Figure 1. Representative 2D spectra of PC645 and PE555 plotted at various waiting times (T) with corresponding linear absorption spectra shown alongside the T = 55 fs spectrum of PC645 and the T = 100 fs spectrum of PE555. The 2D spectra are the real part of the total signal, plotted with 33 evenly-spaced contours. The colored bars in the linear spectra indicate locations of the estimated peak transition energies of individual components.

Figure 1 compares 2DES spectra recorded for PC645 (*Chroomonas* cp. CCMP270) and PE555 (*Hemiselmis andersenii*). These complexes contain different bilins but have a very similar protein structure. Variations in the structure of the proteins (the fascinating ‘open’ versus ‘closed’ structures our collaborators recently discovered by x-ray crystallography [Harrop, et al. in preparation]) lead to the central PEB bilins of PE555 being held much further apart than central DBVs of PC645. This ‘open’ antenna structure reduces the electronic coupling of the central dimer in PE555 compared to the ‘closed’ structures like PC645. Possibly connected with the excitonic dimer, 2D spectra of PC645 show interesting features. In particular, an off diagonal crosspeak that oscillates as a function of waiting time. On the other hand, PE555, which has an ‘open’ structure, shows a fairly round spectrum without distinct cross peaks. The PE555 spectra also oscillate as a function of waiting time but we assigned these oscillations to vibrational wavepackets.

There has been debate over the interpretation of the 2DES experiments. In particular, it has been argued that oscillations due to vibrational coherences can appear very similar to electronic coherences in 2DES data. In a typical photosynthetic protein there are several vibrational modes accessible by stimulated Raman scattering. These modes lead to oscillations in pump-probe and 2DES measurements at very similar frequencies to those reported to be exciton coherences. This has been a significant challenge in the interpretation of the ultrafast measurements. Vibrational coherence refers to pure nuclear wavepacket motion induced by photo-excitation and is characteristic of resonance Raman active normal modes in the molecule on either the ground or excited electronic state. Electronic coherence here refers to the coherent excitation of two electronic states coupled by electronic interactions but uncoupled from any vibrational modes in the system. Assignment of the nature of the modes is critical to a meaningful interpretation of the results. In our most recent work (beyond this first contract period) concluded that these coherences actually work hand-in-hand.

In the AFOSR work, we took a systematic approach to identify and differentiate signatures of different types of coherences present in 2DES data. We distinguished the types of coherences in 3- versus 4-level system. The 3-level system was modelled using a ground state and two electronic excited states, assumed to be excitonic states of the system (e.g. model dimer). A coherent superposition between these two electronic states, signalled by the off-diagonal density elements was considered to give rise to signatures associated to purely electronic coherence between electronic eigenstates. The 4-level system was assumed representative of a single chromophore (2-level system) with an additional vibrational level in both the ground and excited states. In this case vibrational coherence was possible as either a ground-

state vibrational wave packet or as an excited-state vibrational wave packet. Calculation of the dynamics of a 3- and 4-level system provides a good test case for the simplest model of electronic or vibrational coherence. We note that this procedure for discriminating between electronic and vibrational coherences is really only valid in the strong electronic coupling limit.

In further work we measured 2DES spectra for PC645 with very high signal-to-noise, enabling a detailed analysis. This was enabled by the AFOSR funding that helped finance the completely new experimental design and setup. The oscillations of the PC645 cross peak observed below the diagonal were monitored. The oscillations were fit to a sum of eight damped cosine functions, identifying several oscillating components that contribute to the overall signal. The rephasing and nonrephasing contributions were separated and examined independently. Both components showed clear signs of oscillations, albeit similar in general, a Fourier transform of the separate components indicated two modes very close in frequency – 21 THz (700 cm^{-1}) and 26 THz (870 cm^{-1}) - and that one of the frequency components was clearly visible in the rephasing trace while absent in the nonrephasing trace. This work, which other experiments continue to support, showed that an electronic and nuclear coherence are present and are closely matched in frequency.

A review of achievements associated with the AFOSR program concerned with coherence in photosynthetic light harvesting will be published in detail as a "Headline Review" in the Journal of the Royal Society: Interface, as Francesca Fassioli, Rayomond Dinshaw, Paul C. Arpin, and Gregory D. Scholes: "Photosynthetic light harvesting: Excitons and coherence" (submitted 2013).
Abstract: Photosynthesis begins with light harvesting, where specialized pigment-protein complexes transform sunlight into electronic excitations delivered to reaction centers to initiate charge separation. There is evidence that quantum coherence between electronic excited states plays a role in energy transfer. In this review, we discuss how quantum coherence manifests in photosynthetic light harvesting and its implications. We begin by examining the concept of an exciton, an excited electronic state delocalized over several spatially separated molecules, which is the most widely available signature of quantum coherence in light-harvesting. We then discuss recent results concerning the possibility that quantum coherence between electronically excited states of donors and acceptors may give rise to a quantum coherent evolution of excitations, modifying the traditional incoherent picture of energy transfer. Key to this (partially) coherent energy transfer appears to be the structure of the environment, in particular the participation of non-equilibrium vibrational modes. We discuss the open questions and controversies regarding quantum coherent energy transfer, and how these can be addressed with new developing experimental techniques.

General conclusions (Scholes Group): The most important conclusion that we can draw from the vast amount of work over recent years on coherence and coherent dynamics in light harvesting is that both the suggestions by experiments and predictions by theory are accumulating evidence that the mechanisms for energy transfer in light harvesting involves quantum coherence. More surprisingly, evolution appears to be dictated by unitary evolution. The significance of coherent dynamics for light harvesting function is yet unclear and may be subtle, but these effects are likely to nevertheless alter the microscopic picture of energy transfer. Together, all this work is providing a detailed picture for how light harvesting complexes function.

2. Coherence in photosynthetic light harvesting (theoretical)

Fundamental questions that affect the quantum dynamics of molecular systems, and those of interest to light harvesting were addressed in a number of enlightening studies. They can be classified in three categories: (i) the role of coherence in systems excited by natural light (such as sunlight and moonlight) vs. that of coherence induced by pulsed laser light (such as in 2DES); (ii) computational tools to address the issue of the dynamics of electronic dynamics in light harvesting systems, and (iii) the nature of electronic coherence and decoherence in realistic molecular systems. A summary of studies in these inter-related areas is provided below.

(i) Natural Light vs. Coherent Light: As described in the experimental section above, a key observation of 2DES is the occurrence of coherent dynamics in light harvesting systems. However, such experiments utilize pulsed coherent laser light, whereas natural processes take place under incoherent excitation, such as sunlight and moonlight. In several studies, we addressed the differences in molecular response to these different types of incident fields, with the intent of understanding the information content of the 2DES experiments with respect to natural systems. A study of incoherent excitation of arbitrary systems in both the open (dissipative) case or the closed (unitary) case, showed that incoherent

light produces incoherent mixtures of stationary system energy eigenstates after short transient times. Hence, after this short transient time, there is no longer any coherent dynamics. This was the case for both generic molecular systems as well as models of light-induced processes in retinal, an important biological system. In addition, this difference was manifest even on the level of the wavefunction in individual realizations of incoherent light incident on molecules. Hence, the direct inference that the coherences observed in laboratory experiments will be observed in natural processes, is not substantiated. However, the open system study made clear that the incoherence induced by the incoherent light is likely less important than the incoherence induced by the background environment. Further studies of this important competition are underway.

(ii) Computational methods and approaches: Photosynthetic light harvesting systems present unusual computational challenges, since they apply to open quantum systems in a domain where couplings and energy level spacings are of comparable sizes. We have addressed this issue in several publications, which include both a thorough critique of available methods as well as a study of the validity of two popular approximations, the Markov approximation and the second order Born Master equation. Considerable insight was gained into the range of applicability of these methods, with analytic estimates of conditions under which the approximations become invalid. Such studies are of considerable importance, as the search for reliable, efficient and effective computational tools for these open quantum systems continues.

(iii) Understanding Longevity in Electronic Energy Transfer:

(a) The original 2DES experimental results made clear that coherences were lasting far longer than originally anticipated. This implies a far smaller decoherence effect than expected, a result of importance to both light harvesting systems and quantum technologies. To examine such effects in realistic systems, we carried out studies of electronic energy transfer in trans-polyacetylene, a representative molecule with a well established Hamiltonian, but whose electronic coherence properties are poorly understood. Decoherence was found to increase substantially with the increasing size of the system, and to result in electronic coherence times of 10 fs in systems with more than 50 acetylenes in the chain. Several mechanisms for this short time electronic coherence were identified, Further, and most interestingly, highly long lived oscillatory dynamics was observed in polyacetylene for specific initial states. A detailed study of such states showed that, remarkably, although the dynamics showed oscillatory changes in population between exciton states, the dynamics was not coherent! Rather, we identified a bath-induced dynamical effect that periodically, and incoherently, transferred population between exciton levels. This is a totally new effect, that may well affect the interpretation of 2DES experiments, and that motivates the question of whether such effects can be observed and identified via 2DES spectroscopy, and whether they are important to light harvesting systems.

(b) A careful examination of the status of studies of electronic energy transfer showed that, remarkably, the vast majority of studies rely entirely on models for the computation and interpretation of electronic energy transfer. No direct computational approach to following electronic energy transfer, even given the time dependent quantum mechanical wavefunction $|\psi(t)\rangle$, appeared in the literature at the start of this work. However, quantum mechanics does require the existence of an operator O for each observable, with the time evolution of the electronic energy should be given by $\langle\psi(t)|O|\psi(t)\rangle$. However, no such operator O was known. Taking up this challenge we discovered considerable depth to this problem, especially in its relationship to the fundamental requirement for electron antisymmetization over the entire molecule. In particular, attempts to partition the electronic energy within a large molecule led to a fundamental analysis of the role of electron antisymmetrization as it affects partitioning, and the successful introduction of a symmetrized operator O that is applicable both to time independent as well as time dependent states. Applications of this approach to realistic molecular systems are underway.

(c) The surprisingly long coherences observed in photosynthetic light harvesting systems continue to generate vast amounts of research in an effort to understand the origins of this longevity in spite of the apparent opportunity for extensive decoherence. Numerous computational studies seemed to support this result, but provide no insight into its physical origin. To address this issue we examined, analytically, a spin-boson model which successfully captured the essential features of the observations, and provided deep insights into its origins. Specifically, we found that long lived coherences were observed, with many of the characteristics features of the experimental results, when the (1) the spacing between excitonic levels is small, and (2) the ratio of the energy gap to the coupling between excitonic states is small, with the resultant system lying in an effective low temperature regime. This constitutes the first approach that provides analytic insight into the conditions for long lived coherences in open systems of the type involved in photosynthetic light

harvesting.

General Conclusions {Brumer group): Considerable progress has been made in understanding the nature of long-lived molecular coherences induced by pulsed laser sources. Conditions for such long-lived features have been quantified, major problems regarding the effects of electron antisymmetrization and its role in electronic energy transfer have been resolved, studies have been done on energy transfer in realistic molecular systems, and considerable progress has been made on the important question of excitation by natural incoherent light vs. laboratory studies that utilize coherent pulsed laser sources.

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